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DATA EVALUATION REPORT

STUDY TYPE: Leaching (#163-1)

TOX. CHEM. NO.: 129057

TEST COMPOUND: Silver Zinc Zeolite

ACCESSION NO.: 420328-07

ADL REFERENCE NO.: 66365-20

TITLE OF REPORT: Silver Zinc Zeolite: Leaching of Silver and Zinc From Impregnated Polymers

AUTHOR: James N. Kyranos, Ph.D.

DATE: May 31, 1991

SPONSOR: Kanebo Zeolite USA, Inc.

PERFORMING LAB: Arthur D. Little, Inc.; Acorn Park, Cambridge, MA 02140

CONCLUSION: The concentrations of silver in the leachates generated in this study are below U.S.EPA drinking water guideline (50 ug/L) for silver. Taking into account the total zinc concentrations which included the background levels, the total zinc concentration was well below the recommended guideline for zinc in drinking water (500 ug/L).

This rationale for using pH 6.5 was not given. Information on leaching at pH levels above and below pH 6.5 should have been included.

CLASSIFICATION: This study (#163-1) is classified Supplementary, but it can be upgraded upon submission of additional pH information.

COMPLIANCE: A GLP statement was included on page 3 of study.
A Quality Assurance Statement was included on page 4 of the study.
A No Data Confidentiality Claim was included on page 2 of the study.
There was no Flagging statement included.

BACKGROUND: This study was performed "to determine the quantity of soluble silver and zinc released into an aqueous medium from polymeric materials impregnated with silver zinc zeolite".

A. MATERIALS:

Test material: Silver zinc zeolite contained 3.6% silver and 6.1% zinc on a dry weight basis. Zeolite was incorporated into two polymer matrices listed below:

Material PE -- Polyester Non-woven Fabric
Polyethylene terephthalate staple fiber incorporated with silver zinc Zeolite at 1.5% by weight (anhydrous) by mixer kneading. Non-woven production: carding and needle punching.

Material PP -- Polypropylene plate
Polypropylene plate of polypropylene incorporated silver zinc zeolite at 1.5% by weight by extruder kneading. Plate preparation by injection molding.

Negative controls: Consisted of vials containing 30 mL leaching medium (ASTM Type I water), nichrome wire, and glass beads, but no polymeric material test coupons.

Positive controls: Same as negative controls along with a small volume of a standard solution containing silver and zinc ions to give an initial concentration of 10 ppb (ug/L) of silver and 25 ppb (ug/L) of zinc.

Test Exposure System:
This system was designed to allow control of light, temperature and agitation of the test vial's contents. The test was conducted inside a black exposure chamber that had air vents permanently shielded and the top in place except when samples were removed. Temperature was controlled by a circulating water bath set at 25 $\pm$ 0.1°C. The content of each vial was mechanically agitated using a magnetic stir plate.

B. STUDY DESIGN:

Test coupons of non-woven polyester were cut as 1.5 cm x 1.5 cm ($\pm$ 0.1 cm) squares. The coupons were individually weighed and then strung in groups of three onto nichrome wire with glass bead spacers.

Test coupons of the polypropylene plate material were cut (1.5 cm x 1.5 cm) into squares, weighed and then strung into groups of three onto nichrome wire with glass bead spacers.

The coupon assemblies were placed into individual 40-mL glass vials. The leaching medium (30 mL ASTM Type I water) was added to each vial. The initial pH of the medium in each vial was measured and recorded using narrow-range pH paper.

After the vials were placed in the constant temperature water bath, taken as time zero (t_o), samples were withdrawn at intervals of 2, 4, 8, 16, 24 and 30 days (±1 hour), after time zero, for subsequent chemical analysis. The pH was again measured, then a measured quantity of concentrated nitric acid was added to bring the pH below 2. The vials were then stored in the dark in a 4 °C refrigerator before analysis.

Chemical analysis and data reduction:
Graphite Furnace Atomic Absorption Spectroscopy (GFAA) was used to analyze samples of the leachate, negative and positive controls. An external calibration curve based on appropriate standards was generated to help in quantification. Leachate samples were diluted to bring instrumentation response within the documented linear range of the analysis when necessary.

Calibration curves and calculated sample concentrations were based on the average height of the GFAA peak for two sequential analyses of each sample or diluted sample.

C. RESULTS:

Results of leaching tests for negative controls (Table 1 appended):
According to protocol, the data quality objective for the negative controls should be <5X the Level of Quantification (LOQ) for silver and <1X LOQ for zinc. After the calibration standards were measured, the analytical LOQ was determined to be 0.30 ppb for silver and 20 ppb for zinc. Therefore, all negative controls in this study had concentrations below the LOQ.

Results of leaching tests for positive controls (Table 2 appended):
The analysis of positive controls, which were spiked with 10 ppb (ug/L) silver and 25 ppb (ug/L) zinc, show that the percent of silver recovered met the protocol objective of 70-120%. The results for zinc do not meet the quality objective of the protocol. The author cites two reasons for this: 1) the relatively large background zinc concentration might not have been adequately represented by the daily blank samples, and 2) it may be related to the analytical procedure. Other possibilities include the improper preparation of the spiking solution, and/or improperly cleaned glassware.

Results of tests for polyester fabric material (Tables 4-5 appended):
The pH of the solution was constant throughout the study, except

for day 30. Although it was lower on this day, it did not appear to have an effect on the results. For each day sampling, the results for silver determination (Table 4) indicate that the Data Quality Objective of ± 20% RPD/RSD were met. Two of the duplicate samples were lower than expected and were considered outliers.

(Note: $RPD\ (5) = 100 \times \frac{\text{Difference between high and low value}}{\text{Mean of the values}}$

$RSD\ (\%) = 100 \times \frac{\text{Standard Deviation (n-1 basis)}}{\text{Mean of the values}}$

The corresponding results for leaching of zinc were considerably higher than expected when compared to the silver results. This was indicative of a large zinc background that should be proven as such.

Results of Leaching Tests for Polypropylene Plate Material (Tables 7 and 8 appended) :
The results of the silver leachate data suggest that the silver concentration is maintained at an average concentration of 0.0038 ug/g (35 ng/cm^2) throughout the study.

The results of the zinc leachate data show that there is a higher amount of zinc being leached than expected. The Author attributed the large amount zinc levels to background interferences. Unless there is proof of this, it has to be assumed that the zinc levels are legitimate.

Discussion\Conclusion:

-The results of this study show that over a 30 day period, a clear trend is shown in regard to the leachability of silver from silver zinc zeolite impregnated polymers. Silver leached at a relatively constant rate throughout the study at 0.0038 ug/g (0.0035 ng/cm^2) of polymeric material.

-Initially (Day 0-4), the amount of silver leached from the polyester fabric was 0.48 ug/mg polymeric material. After the fourth day, it had reached an average concentration of 2.30 ug/g.

-The Author states that there was uncertainty about the concentration of zinc released from each polymeric material due to the high background interference. However, the actual background level cannot be confirmed.

-The concentrations silver in the leachates generated in this study are below U.S.EPA drinking water guideline requirements (50 ug/L) for silver. Taking into account the total zinc concentrations which included the background levels, the total zinc concentration

was well below the recommended guideline for zinc in drinking water (500 ug/L).

This rationale for using pH 6.5 was not given. Information on leaching at pH levels above and below pH 6.5 should have been included. This study (#163-1) is classified Supplementary, but it can be upgraded upon submission of this information.

Table 1 - Results for Leaching Study Negative Control (Blank) Samples

SAMPLE	INITIAL pH	TEST DAY	TEST DATE	FINAL pH	ANALYSIS DATE	SILVER (ppb)	ANALYSIS DATE	ZINC (ppb)
BL-0	6.5	0	4/1/91	6.5	4/3/91	ND	4/9/91	8.9
BL-2	6.5	2	4/3/91	6.5	4/3/91	ND	4/9/91	17.3
BL-4	6.5	4	4/5/91	6.5	4/9/91	ND	4/9/91	95.9
BL-8	6.5	8	4/9/91	6.5	4/9/91	ND	4/9/91	95.2
BL-16	6.5	16	4/17/91	6.5	4/22/91	ND	4/29/91	7.7
BL-24	6.5	24	4/25/91	6.5	4/26/91	ND	4/29/91	14.6
BL-30	6.5	30	5/1/91	5.3	5/15/91	ND	5/15/91	12.9

LOQ < 5X for - < 100

ND - Not Detected (sample response in laboratory blank range)

NC S/N < 5X LOQ

Ag LOQ = $\frac{30 \text{ ppb} \times \frac{5}{1.50}}{}$

Zn LOQ = $\frac{20 \text{ ppb} \times \frac{5}{100}}{}$

Table 2 - Results for Analysis of Leaching Study Positive Control (Spike) Samples

SAMPLE	INITIAL pH	TEST DAY	TEST DATE	FINAL pH	ANALYSIS DATE	DILUT FACTOR	SILVER (ppb)	ZINC (ppb)**	PERCENT RECOVERY SILVER %	PERCENT RECOVERY ZINC %
SP-0-AG	6.5	0	4/1/91	6.5	4/3/91		9.9		99	
SP-0-AG	6.5	0	4/1/91	6.5	4/3/91	1:4	13.0		130	
SP-2-AG	6.5	2	4/3/91	6.5	4/3/91		8.2		82	
SP-2-AG	6.5	2	4/3/91	6.5	4/3/91	1:4	10.0		100	
SP-4-AG	6.5	4	4/5/91	6.5	4/9/91		9.4		94	
SP-4-AG	6.5	4	4/5/91	6.5	4/9/91	1:4	10.3		103	
SP-8-AG	6.5	8	4/9/91	6.5	4/9/91		10.5		105	
SP-8-AG	6.5	8	4/9/91	6.5	4/9/91	1:4	12.1		121	
SP-16-AG	6.5	16	4/17/91	6.5	4/22/91		7.9		79	
SP-16-AG	6.5	16	4/17/91	6.5	4/22/91	1:4	9.0		90	
SP-24-AG	6.5	24	4/25/91	6.5	4/26/91		8.8		88	
SP-24-AG	6.5	24	4/25/91	6.5	4/26/91	1:4	10.3		103	
SP-30-AG	6.5	30	5/1/91	5.3	5/15/91		7.9		79	
SP-30-AG	6.5	30	5/1/91	5.3	5/15/91	1:4	11.6		116	
SP-0-ZN	6.5	0	4/1/91	6.5	4/3/91			56.5		226
SP-2-ZN	6.5	2	4/3/91	6.5	4/3/91			47.5		190
SP-4-ZN	6.5	4	4/5/91	6.5	4/9/91			67.3		270
SP-8-ZN	6.5	8	4/9/91	6.5	4/9/91			70.8		284
SP-16-ZN	6.5	16	4/17/91	6.5	4/29/91			53.4		214
SP-24-ZN	6.5	24	4/25/91	6.5	4/29/91			48.5		194
SP-30-ZN	6.5	30	5/1/91	5.3	5/15/91			56.5		226

** - Corrected for blank concentration on corresponding day

Table 4 - Silver Concentration Data for Polyester Fabric Leachates

				SILVER						
SAMPLE	TEST DAY	ANALYSIS DATE	DILUTION	SOL'N CONC (ppb)	AMNT RELSED (ug/g)	AVERAGE (ug/g)	RPD/RSD	AMNT RELSED (ng/cm2)	AVERAGE (ng/cm2)	RPD/RSD
PE-0A	0	4/3/91		1.81	0.48			2.53		
						0.48	2		2.52	0.8
PE-0B	0	4/3/91		1.73	0.47			2.51		
PE-2A	2	4/3/91		4.36	1.06			6.09		
PE-2A	2	4/3/91	1:2	4.44	1.08			6.20		
						1.14	8		6.26	5
PE-2B	2	4/3/91		4.67	1.14			6.07		
PE-2B	2	4/3/91	1:2	5.14	1.26			6.68		
PE-4A	4	4/9/91		7.01	2.01			9.79		
PE-4A	4	4/9/91	1:4	6.49	1.86			9.06		
						1.96	6		9.60	6
PE-4B	4	4/9/91		7.15	2.10			10.34		
PE-4B	4	4/9/91	1:4	6.37	1.87			9.21		
PE-8A	8	4/9/91		9.01	2.15			12.58		
PE-8A	8	4/9/91	1:4	9.93	2.37			13.87		
						2.34	6		12.76	6
PE-8B	8	4/9/91		8.92	2.46			12.46		
PE-8B	8	4/9/91	1:4	8.67	2.39			12.11		

* - Outlier not used in calculation of average

DQO ±20% RPD/RSD

Table 4 - Silver Concentration Data for Polyester Fabric Leachates (Continued)

SILVER

SAMPLE	TEST DAY	ANALYSIS DATE	DILUTION	SOL'N CONC (ppb)	AMNT RELSED (ug/g)	AVERAGE (ug/g)	RPD/RSD	AMNT RELSED (ng/cm2)	AVERAGE (ng/cm2)	RPD/RSD
PE-16A	16	4/22/91		8.09	2.07			11.72		
PE-16A	16	4/22/91	1:4	9.02	2.31			13.07		
						2.20	7		12.31	7
PE-16B	16	4/22/91		7.85	2.04			11.38		
PE-16B	16	4/22/91	1:4	9.02	2.36			13.07		
PE-24A	24	4/26/91		4.67	1.17*			6.77*		
PE-24A	24	4/26/91	1:2	4.39	1.10*			6.36*		
PE-24B	24	4/26/91		8.87	2.48			12.85		
PE-24B	24	4/26/91	1:4	9.64	2.69	2.59	8	13.97	13.41	8
PE-30A	30	5/15/91		2.91	0.69*			4.01*		
PE-30A	30	5/15/91	1:4	3.25	0.76*			4.48*		
PE-30B	30	5/15/91		7.43	2.05			10.77		
PE-30B	30	5/15/91	1:4	9.10	2.51	2.29	20	13.19	11.98	20

* - Outlier not used in calculation of average

Table 5 - Zinc Concentration Data for Polyester Fabric Leachates

ZINC

SAMPLE	TEST DAY	ANALYSIS DATE	DILUTION	SOL'N CONC (ppb)
PE-0A	0	4/9/91		12.4
PE-0B	0	4/9/91		9.9
PE-2A	2	4/9/91		11.0
PE-2B	2	4/9/91		31.6
PE-4A	4	4/9/91		101.8
PE-4B	4	4/9/91		80.4
PE-8A	8	4/9/91		104.3
PE-8B	8	4/9/91		99.7
PE-16A	16	4/29/91		49.4
PE-16B	16	4/29/91		49.4
PE-24A	24	4/29/91		62.1
PE-24B	24	4/29/91		60.1
PE-30A	30	5/15/91		62.2
PE-30B	30	5/15/91		68.5

Table 7 - Silver Concentration Data for Polypropylene Plate Leachates

				SILVER					
SAMPLE	TEST DAY	ANALYSIS DATE	DILUTION	SOL'N CONC (ppb)	AMNT RELSED (ug/g)	AVERAGE (ug/g)	RPD/RSD	AMNT RELSED (ng/cm2)	AVERAGE (ng/cm2)	RPD/RSD
PP-0A	0	4/3/91		0.60	0.010*			0.94		
PP-0A	0	4/9/91		0.31	0.0051			0.49		
						0.0052	12		0.48	12
PP-0B	0	4/3/91		0.35	0.0058			0.54		
PP-0B	0	4/9/91		0.28	0.0046			0.43		
PP-2A	2	4/3/91		0.36	0.0060			0.56		
						0.0056	16		0.52	17
PP-2B	2	4/3/91		0.31	0.0051			0.47		
PP-4A	4	4/9/91		0.15	0.0024			0.23		
						0.0020	45		0.19	47
PP-4B	4	4/9/91		0.090	0.0015			0.14		
PP-8A	8	4/9/91		0.090	0.0015			0.14		
						0.0014	14		0.13	15
PP-8B	8	4/9/91		0.076	0.0013			0.12		
PP-16A	16	4/22/91		0.25	0.0040			0.37		
						0.0029	79		0.27	78
PP-16B	16	4/22/91		0.10	0.0017			0.16		
PP-24A	24	4/26/91		0.27	0.0045			0.41		
PP-24A	24	4/26/91		0.15	0.0025	0.0035	57	0.23	0.33	55
PP-24B	24	4/26/91		0.037	0.00062*			0.057*		
PP-30A	30	5/15/91		0.46	0.00076			0.071		
						0.0059	174		0.54	172
PP-30B	30	5/15/91		0.65	0.011			1.00		

* - Outlier not used in calculation of average

Table 8 - Zinc Concentration Data for Polypropylene Plate Leachates

ZINC

SAMPLE	TEST DAY	ANALYSIS DATE	DILUTION	SOL'N CONC (ppb)
PP-0A	0	4/9/91		11.0
PP-0B	0	4/9/91		9.6
PP-2A	2	4/9/91		117.6
PP-2B	2	4/9/91		97.6
PP-4A	4	4/9/91		99.7
PP-4B	4	4/9/91		101.5
PP-8A	8	4/9/91		120.1
PP-8B	8	4/9/91		138.7
PP-16A	16	4/29/91		19.7
PP-16B	16	4/29/91		23.9
PP-24A	24	4/29/91		18.4
PP-24B	24	4/29/91		27.3
PP-30A	30	5/15/91		20.2
PP-30B	30	5/15/91		16.8